

PATENT APPLICATION
FOR
CATALYSTS, METAL COMPLEXES, COMPOSITIONS
AND ARRAYS CONTAINING ERBIUM

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PATENT

CATALYSTS, METAL COMPLEXES, COMPOSITIONS AND
ARRAYS CONTAINING ERBIUM

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 60/181,123, filed February 8, 2000, which is incorporated herein by reference for all purposes.

FIELD OF THE INVENTION

[0002] The present invention relates to new compositions that provide useful catalysts for polymerizations, with such catalysts containing erbium.

BACKGROUND OF THE INVENTION

[0003] Ancillary (or spectator) ligand-metal coordination complexes (e.g., organometallic complexes) and compositions are useful as catalysts, additives, stoichiometric reagents, monomers, solid state precursors, therapeutic reagents and drugs. Ancillary ligand-metal coordination complexes of this type can be prepared by combining an ancillary ligand with a suitable metal compound or metal precursor in a suitable solvent at a suitable temperature. The ancillary ligand contains functional groups that bind to the metal center(s), remain associated with the metal center(s), and therefore provide an opportunity to modify the steric, electronic and chemical properties of the active metal center(s) of the complex.

[0004] Certain known ancillary ligand-metal complexes and compositions are catalysts for reactions such as oxidation, reduction, hydrogenation, hydrosilylation, hydrocyanation, hydroformylation, polymerization, carbonylation, isomerization, metathesis, carbon-hydrogen activation, carbon-halogen activation, cross-coupling, Friedel-Crafts acylation and alkylation, hydration, dimerization, trimerization, oligomerization, Diels-Alder reactions and other transformations.

[0005] One example of the use of these types of ancillary ligand-metal complexes and compositions is in the field of polymerization catalysis. In connection with single site catalysis, the ancillary ligand offers opportunities to modify the electronic and/or steric environment surrounding an active metal center. This allows the ancillary ligand to assist in the creation of possibly different polymers.

[0006] Lanthanide based catalysts are generally known for polymerization reactions.

See, generally, Anwander, R. in "Applied Homogeneous Catalysis with Organometallic Compounds", Cornils B., Herrmann W. A., Eds. (VCH Publishers, New York, 1996), Vol. 2, Section 3.2.5, pp. 866-892 and the references therein and

Marks et al., *Organometallics*, 1999, vol. 18, pp. 2568-2570 and the references therein, all of which is incorporated herein by reference. Although erbium based catalysts have been tested in limited circumstances, they are generally considered to have low activity with respect to other lanthanide-based catalysts. See, "New coordination catalysts based on rare earth compounds for the polymerization of 1-octene", Yang, et al., *J. Polym. Sci, Part A, Polym. Chem.*, 1992, vol. 30, pp. 63-69; "Progress in Coordination Polymerization by Rare Earth Catalysts", Shen, *Inorganica Chimica Acta*, 1987, vol. 140, pp. 7-14; and Ouyang, et al, *Proc. China-U.S. Bilateral Symp. Poly. Chem. Phys.* (1981), Meeting Date 1979, pp. 382-398; each of which is incorporated herein by reference. Despite these advances, higher activity of Er based catalysts has not been previously demonstrated for monomers of interest commercially. Indeed, the data presented in these cited papers suggests to those of skill in the art that Er based catalysts are not generally promising as catalysts for the polymerization of olefins, diolefins, or acetylenically unsaturated monomers. See also U.S. Patent No. 4,057,565, which is incorporated herein by reference.

[0007] Surprisingly, it has now been discovered that Er based polymerization catalysts are particularly active. In addition, it is always a desire to discover new catalysts that will catalyze or assist in catalysis of reactions differently from known systems. This invention provides new catalyst compositions and complexes that catalyze polymerization reactions more efficiently and selectively than known systems.

SUMMARY OF THE INVENTION

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[0008] The invention disclosed herein are new catalysts comprising metal-ligand complexes or compositions of metal precursors and activators (optionally with ligands) that catalyze polymerization and copolymerization reactions, particularly with monomers that are olefins, diolefins or acetylenically unsaturated. These compositions can also polymerize monomers that have polar functionalities in homopolymerizations or copolymerizations. Also, diolefins in combination with ethylene or α -olefins or 1,1-disubstituted olefins may be co-polymerized. The new catalyst compositions are prepared by combining a metal precursor with a suitable activator and, optionally, a suitable ligand. The main feature of this invention is the use of erbium to provide the active polymerization metal center. Erbium has been investigated as a polymerization catalyst with certain ligands (see Ballard et al., *J. Chem. Soc., Chem. Comm.*, **1978**, 994-995 or US. Patent 4,057,565, which are both incorporated herein by reference). However, the general utility of erbium as an active polymerization metal center was not previously disclosed, until this invention.

[0009] Thus, it is an object of this invention to provide polymerization catalysts that use erbium as the active metal center.

[0010] It is a further object of this invention to polymerize olefins and acetylenically unsaturated monomers with a catalyst comprised of an erbium compound or complex.

[0011] It is still a further object of this invention to polymerize olefins and acetylenically unsaturated monomers with a catalyst composition that comprises an erbium compound or complex and an activator or combination of activators.

[0012] Metal complexes, compositions or compounds using erbium and one or more ligands are within the scope of this invention. Many ligands and activators form useful polymerization catalysts with an erbium metal precursor for polymerization. Moreover, the erbium complex may be in a neutral or charged state. Thus, the erbium compounds or complexes may take may different forms, for example they may be monomeric, dimeric or higher orders thereof.

[0013] In another aspect of the invention, a polymerization process is disclosed for monomers. The polymerization process involves subjecting one or more monomers to the catalyst compositions or complexes of this invention under polymerization

conditions. The polymerization process can be continuous, batch or semi-batch and can be homogeneous, supported homogeneous or heterogeneous.

[0014] Further aspects of this invention will be evident to those of skill in the art upon review of this specification.

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DETAILED DESCRIPTION OF THE INVENTION

[0015] The inventions disclosed herein include metal complexes and compositions, which are useful as catalysts for polymerization reactions.

10 **[0016]** As used herein, the phrase “characterized by the formula” is not intended to be limiting and is used in the same way that “comprising” is commonly used. The term “independently selected” is used herein to indicate that the R groups, e.g., R¹, R², R³, R⁴, and R⁵ can be identical or different (e.g. R¹, R², R³, R⁴, and R⁵ may all be substituted alkyls or R¹ and R² may be a substituted alkyl and R³ may be an aryl, etc.).

15 A named R group will generally have the structure that is recognized in the art as corresponding to R groups having that name. The terms “compound” and “complex” are generally used interchangeably in this specification, but those of skill in the art may recognize certain compounds as complexes and vice versa. For the purposes of illustration, representative certain groups are defined herein. These definitions are
20 intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

[0017] The term “alkyl” is used herein to refer to a branched or unbranched, saturated or unsaturated acyclic hydrocarbon radical. Suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), vinyl, n-butyl, t-
25 butyl, i-butyl (or 2-methylpropyl), etc. In particular embodiments, alkyls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

[0018] “Substituted alkyl” refers to an alkyl as just described in which one or more hydrogen atom to any carbon of the alkyl is replaced by another group such as a
30 halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, and combinations thereof. Suitable substituted alkyls include, for example, benzyl, trifluoromethyl and the like.

[0019] The term "heteroalkyl" refers to an alkyl as described above in which one or more hydrogen atoms to any carbon of the alkyl is replaced by a heteroatom selected from the group consisting of N, O, P, B, S, Si, Sb, Al, Sn, As, Se and Ge. The bond between the carbon atom and the heteroatom may be saturated or unsaturated. Thus, an alkyl substituted with a heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, or seleno is within the scope of the term heteroalkyl. Suitable heteroalkyls include cyano, benzoyl, 2-pyridyl, 2-furyl and the like.

[0020] The term "cycloalkyl" is used herein to refer to a saturated or unsaturated cyclic non-aromatic hydrocarbon radical having a single ring or multiple condensed rings. Suitable cycloalkyl radicals include, for example, cyclopentyl, cyclohexyl, cyclooctenyl, bicyclooctyl, etc. In particular embodiments, cycloalkyls have between 3 and 200 carbon atoms, between 3 and 50 carbon atoms or between 3 and 20 carbon atoms.

[0021] "Substituted cycloalkyl" refers to cycloalkyl as just described including in which one or more hydrogen atom to any carbon of the cycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted cycloalkyl radicals include, for example, 4-dimethylaminocyclohexyl, 4,5-dibromocyclohept-4-enyl, and the like.

[0022] The term "heterocycloalkyl" is used herein to refer to a cycloalkyl radical as described, but in which one or more or all carbon atoms of the saturated or unsaturated cyclic radical are replaced by a heteroatom such as nitrogen, phosphorous, oxygen, sulfur, silicon, germanium, selenium, or boron. Suitable heterocycloalkyls include, for example, piperazinyl, morpholinyl, tetrahydropyranyl, tetrahydrofuranlyl, piperidinyl, pyrrolidinyl, oxazolinyl and the like.

[0023] "Substituted heterocycloalkyl" refers to heterocycloalkyl as just described including in which one or more hydrogen atom to any atom of the heterocycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino,

silyl, thio, seleno and combinations thereof. Suitable substituted heterocycloalkyl radicals include, for example, N-methylpiperazinyl, 3-dimethylaminomorpholinyl and the like.

[0024] The term "aryl" is used herein to refer to an aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The aromatic ring(s) may include phenyl, naphthyl and biphenyl, among others. In particular embodiments, aryls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

[0025] "Substituted aryl" refers to aryl as just described in which one or more hydrogen atom to any carbon is replaced by one or more functional groups such as alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, alkylhalos (e.g., CF₃), hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in benzophenone or oxygen as in diphenylether or nitrogen in diphenylamine.

[0026] The term "heteroaryl" as used herein refers to aromatic rings in which one or more carbon atoms of the aromatic ring(s) are replaced by a heteroatom(s) such as nitrogen, oxygen, boron, selenium, phosphorus, silicon or sulfur. Heteroaryl refers to structures that may be a single aromatic ring, multiple aromatic ring(s), or one or more aromatic rings coupled to one or more non-aromatic ring(s). In structures having multiple rings, the rings can be fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in phenyl pyridyl ketone. As used herein, rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "heteroaryl."

[0027] "Substituted heteroaryl" refers to heteroaryl as just described including in which one or more hydrogen atoms to any atom of the heteroaryl moiety is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl,

thio, seleno and combinations thereof. Suitable substituted heteroaryl radicals include, for example, 4-N,N-dimethylaminopyridine.

[0028] The term "alkoxy" is used herein to refer to the $-OZ^1$ radical, where Z^1 is selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, silyl groups and combinations thereof as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, benzyloxy, t-butoxy, etc. A related term is "aryloxy" where Z^1 is selected from the group consisting of aryl, substituted aryl, heteroaryl, substituted heteroaryl, and combinations thereof. Examples of suitable aryloxy radicals include phenoxy, substituted phenoxy,

[0029] 2-pyridinoxy, 8-quinolinoxy and the like.

[0030] As used herein the term "silyl" refers to the $-SiZ^1Z^2Z^3$ radical, where each of Z^1 , Z^2 , and Z^3 is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

[0031] As used herein the term "boryl" refers to the $-BZ^1Z^2$ group, where each of Z^1 and Z^2 is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

[0032] As used herein, the term "phosphino" refers to the group $-PZ^1Z^2$, where each of Z^1 and Z^2 is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof.

[0033] The term "amino" is used herein to refer to the group $-NZ^1Z^2$, where each of Z^1 and Z^2 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0034] The term "thio" is used herein to refer to the group $-SZ^1$, where Z^1 is selected from the group consisting of hydrogen; alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0035] The term "seleno" is used herein to refer to the group $-\text{SeZ}^1$, where Z^1 is selected from the group consisting of hydrogen; alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0036] The term "saturated" refers to lack of double and triple bonds between atoms of a radical group such as ethyl, cyclohexyl, pyrrolidinyl, and the like.

[0037] The term "unsaturated" refers to the presence one or more double and triple bonds between atoms of a radical group such as vinyl, acetylide, oxazoliny, cyclohexenyl, acetyl and the like.

Catalytic Compositions

[0038] The main feature of this invention is the use of an erbium compound or complex as a polymerization catalyst or as a component in a composition that is a polymerization catalyst. A first embodiment of this invention is a catalytic polymerization reaction carried out using a catalytic composition, where the composition is comprised of an erbium metal precursor and a suitable polymerization activator or activating technique. In a preferred embodiment, the activator is a combination of an aluminum alkyl compound and an ionic complex that comprises a compatible, non-interfering anion. The catalytic composition may optionally include at least one ligand.

[0039] The metal precursors of this invention are erbium compounds that may be represented by the general formula ErR_3 , meaning that there are three R groups attached to the erbium metal. Each R group may independently be selected from the group consisting of halide (e.g., Cl, F, I or Br), alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, cyclopentadienyl, substituted cyclopentadienyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, hydride, thio, seleno, phosphino, amino, carboxylates, 1,3-dionates, oxalates, carbonates, nitrates, sulfates, perchlorates, sulfonates phosphonates and combinations thereof. In other embodiments, each R is independently selected from the group consisting of halide, hydride, alkyl, substituted alkyl, aryl, substituted aryl, heteroalkyl, cyclopentadienyl,

substituted cyclopentadienyl, silyl, carboxylates, 1,3-dionates, sulfonates and amino. In some embodiments, it is preferred that no two R groups are each cyclopentadienyl or alkyl-substituted or silyl-substituted cyclopentadienyl. Additional discussion of suitable R groups may be found in Schaverien "Organometallic Chemistry of the Lanthanides," *Advances in Organometallic Chemistry*, 1994, vol. 36, pp. 283-362, which is incorporated herein by reference.

[0040] In some preferred embodiments, the erbium metal precursor is a homoleptic compound, meaning that each R group is the same. Such preferred embodiments include those where each R group is the same and selected from the halide, hydride, alkyl, substituted alkyl, aryl, substituted aryl, heteroalkyl, alkoxy, aryloxy, 1,3-dionates, carboxylates and amino.

[0041] Particularly preferred are those erbium precursors having bulky R groups, which are preferred because such bulky groups tend to provide additional stabilization against degradation, and increase solubility. Bulky R groups include groups such as trimethylsilyl-substituted alkyl groups (such as mono-, bis-, and tris-(trimethylsilyl)methyl), alkoxy (such as tert-butoxy), aryloxy (such as 2,6-bis(tert-butyl)phenoxy), bulky amino (such as N,N-bis(trimethylsilyl)amino) and 1,3-dionates (including the substituted versions thereof, such as 2,2,6,6-tetramethyl-3,5-heptanedionate). Also, for additional examples of bulky R groups for the homoleptic erbium metal precursors, those of skill in the art can find additional information in Schaverien "Organometallic Chemistry of the Lanthanides," *Advances in Organometallic Chemistry*, 1994, vol. 36, pp. 283-362, which is incorporated herein by reference. In addition, it is within the scope of this invention to have substituents on the R groups that provide additional stability to the erbium metal center, such as via an amino substituent. In some preferred embodiments, all three R groups are not a naphthenate having the structure $C_5H_9(CH_2)_n-COO^-$, where n is an integer greater than zero. In some preferred embodiments, all three R groups are not a 2-dialkylaminobenzyl or a 2-dialkylaminomethylphenyl.

[0042] In addition to the three R groups attached to the erbium metal precursor, additional neutral groups may be attached to the erbium, designated L herein. Each L group attached to the erbium may be selected from the group consisting of carbon monoxide, isocyanide, nitrous oxide, PA_3 , NA_3 , OA_2 , SA_2 , SeA_2 , and combinations

thereof, wherein each A is independently selected from a group consisting of alkyl, substituted alkyl, heteroalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, and silyl. Optionally, two or more A groups may be linked to form one or more ring structures with the other atoms; thus, for example, OA₂ includes tetrahydrofuran, and bicyclic rings are included. The number of L groups is dependent on each of the groups chosen for R, but theoretically there may be up to five L groups attached to the erbium atom in the metal precursor, meaning that 0, 1, 2, 3, 4 or 5 L groups may be datively bonded to the Er atom. Additionally, two or more L groups may connected together with a linking group to form chelating neutral groups (for example, N,N,N',N'-tetramethylethylenediamine).

[0043] In yet other embodiments, the erbium metal precursor may be an ionic complex with an appropriate counter balancing charge from one or more counterions. Thus, ErR₄⁻ is within the scope of this invention with an appropriate counter balancing cation, such as Li(OA₂)_n⁺ (with the previous definition of n), giving for example, Er(tert-butyl)₄⁻ Li(O(C₂H₅)₂)₄⁺ or Er(CH₃)₆³⁻ (Li(N,N,N',N'-tetramethylethylenediamine)⁺)₃

[0044] Although a general erbium metal precursor definition was just provided, the erbium may be provided to the catalytic composition as a metal atom, ion, compound or other metal precursor compound. In many applications, the compositions of this invention will be combined and the product of such combination is not determined, if a product indeed forms. For example, the components of the composition may or may not be added to a reaction vessel at the same time as the reactants, i.e., monomers or other polymerization reaction components (e.g., such as scavengers, solvents, etc.).

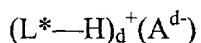
Polymerization Activators/Additives

[0045] The erbium metal precursors are active catalysts in combination with a suitable activator or activating technique, and optionally one or more ligands. Broadly, the activator may comprise alumoxanes, Lewis acids, Bronsted acids, compatible non-interfering activators and combinations of the foregoing. The foregoing activators have been taught for use with different compositions or metal complexes in the following references, which are hereby incorporated by reference in

their entirety: U.S. Patents 5,599,761, 5,616,664, 5,453,410, 5,153,157, 5,064,802, and EP-A-277,004. In particular, ionic or ion forming activators are preferred.

[0046] Suitable ion forming compounds useful as an activator in one embodiment of the present invention comprise a cation which is a Bronsted acid capable of donating a proton, and an inert, compatible, non-interfering, anion, A^- . Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core. Mechanistically, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions that comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

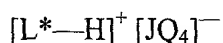
[0047] Preferably such activators may be represented by the following general formula:



wherein, L^* is a neutral Lewis base; $(L^*—H)^+$ is a Bronsted acid; A^{d-} is a non-interfering, compatible anion having a charge of d^- , and d is an integer from 1 to 3.

More preferably A^{d-} corresponds to the formula: $[M^{3+} Q_h]^{d-}$ wherein h is an integer from 4 to 6; $h-3 = d$; M' is an element selected from Group 13 of the Periodic Table of the Elements; and Q is independently selected from the group consisting of hydride, dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, and substituted-hydrocarbyl radicals (including halosubstituted hydrocarbyl, such as perhalogenated hydrocarbyl radicals), said Q having up to 20 carbons. In a more preferred embodiment, d is one, i.e., the counter ion has a single negative charge and corresponds to the formula A^- .

[0048] Activators comprising boron or aluminum which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



wherein: L^* is as previously defined; J is boron or aluminum; and Q is a fluorinated

C₁₋₂₀ hydrocarbonyl group. Most preferably, Q is independently selected from the group selected from the group consisting of fluorinated aryl group, especially, a pentafluorophenyl group (i.e., a C₆F₅ group) or a 3,5-bis(CF₃)₂C₆H₃ group.

Illustrative, but not limiting, examples of boron compounds which may be used as an

5 activating cocatalyst in the preparation of the improved catalysts of this invention are

tri-substituted ammonium salts such as: trimethylammonium tetraphenylborate,

triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-

butyl)ammonium tetraphenylborate, tri(t-butyl)ammonium tetraphenylborate, N,N-

dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-

10 dimethylanilinium tetra-(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-

trimethylanilinium) tetraphenylborate, trimethylammonium

tetrakis(pentafluorophenyl) borate, triethylammonium tetrakis(pentafluorophenyl)

borate, tripropylammonium tetrakis(pentafluorophenyl) borate, tri(n-butyl)ammonium

tetrakis(pentafluorophenyl) borate, tri(secbutyl)ammonium

15 tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium

tetrakis(pentafluorophenyl) borate, N,N-diethylanilinium tetrakis(pentafluorophenyl)

borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl) borate,

trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate and N,N-

dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl) borate; dialkyl ammonium salts

20 such as: di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, and

dicyclohexylammonium tetrakis(pentafluorophenyl) borate; and tri-substituted

phosphonium salts such as: triphenylphosphonium tetrakis(pentafluorophenyl) borate,

tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and tri(2,6-

dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate; and N,N-

25 dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate. Preferred [L*—H]⁺

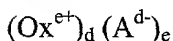
cations are N,N-dimethylanilinium and tributylammonium. Preferred anions are

tetrakis(3,5-bis(trifluoromethyl)phenyl)borate and tetrakis(pentafluorophenyl)borate.

In some embodiments, the most preferred activator is PhNMe₂H⁺B(C₆F₅)₄⁻.

[0049] Other suitable ion forming activators comprise a salt of a cationic oxidizing

30 agent and a non-interfering, compatible anion represented by the formula:



wherein: Ox^{e+} is a cationic oxidizing agent having a charge of e⁺; e is an integer from

1 to 3; and A^{d-} , and d are as previously defined. Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+ , or Pb^{+2} . Preferred embodiments of A^{d-} are those anions previously defined with respect to the Bronsted acid containing activating cocatalysts, especially

5 tetrakis(pentafluorophenyl)borate.

[0050] Another suitable ion forming, activating cocatalyst comprises a compound which is a salt of a carbenium ion or silyl cation and a non-interfering, compatible anion represented by the formula:



10 wherein: C^+ is a C_{1-100} carbenium ion or silyl cation; and A^- is as previously defined. A preferred carbenium ion is the trityl cation, i.e. triphenylcarbenium. The silyl cation may be characterized by the formula $Z^1Z^2Z^3Si^+$ cation, where each of Z^1 , Z^2 , and Z^3 is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl,
15 substituted heteroaryl and combinations thereof. In some embodiments, a most preferred activator is $Ph_3C^+B(C_6F_5)_4^-$.

[0051] In addition, suitable activators include Lewis acids, such as those selected from the group consisting of tris(aryl)boranes, tris(substituted aryl)boranes, tris(aryl)alanes, tris(substituted aryl)alanes, including activators such as
20 tris(pentafluorophenyl)borane. Other useful ion forming Lewis acids include those having two or more Lewis acidic sites, such as those described in WO 99/06413 or Piers, et al. "New Bifunctional Perfluoroaryl Boranes: Synthesis and Reactivity of the *ortho*-Phenylene-Bridged Diboranes 1,2- $[B(C_6F_5)_2]_2C_6X_4$ ($X = H, F$)", *J. Am. Chem. Soc.*, **1999**, 121, 3244-3245, both of which are incorporated herein by reference.

25 Other useful Lewis acids will be evident to those of skill in the art. In general, the group of Lewis acid activators are within the group of ion forming activators (although exceptions to this general rule can be found) and the group tends to exclude the group 13 reagents listed below. Combinations of ion forming activators may be used.

30 **[0052]** Other general activators or compounds useful in a polymerization reaction may be used. These compounds may be activators in some contexts, but may also serve other functions in the polymerization system, such as alkylating an erbium

metal center or scavenging impurities. These compounds are within the general definition of "activator," but are not considered herein to be ion forming activators. These compounds include a group 13 reagent that may be characterized by the formula $G^{13}R'_{3-p}D_p$ where G^{13} is selected from the group consisting of Al, B, Ga, In and combinations thereof, p is 0, 1 or 2, each R' is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic and combinations thereof, and each D is independently selected from the group consisting of halide, hydride, alkoxy, aryloxy, amino, thio, phosphino and combinations thereof. In other embodiments, the group 13 activator is an oligomeric or polymeric alumoxane compound, such as methylalumoxane and the known modifications thereof. In other embodiments, a divalent metal reagent may be used that is defined by the general formula $M'R'_{2-p}D_p$ and p' is 0 or 1 in this embodiment and R' and D are as defined above. M' is the metal and is selected from the group consisting of Mg, Ca, Sr, Ba, Zn, Cd and combinations thereof. In still other embodiments, an alkali metal reagent may be used that is defined by the general formula $M''R'$ and in this embodiment R' is as defined above. M'' is the alkali metal and is selected from the group consisting of Li, Na, K, Rb, Cs and combinations thereof. Additionally, hydrogen and/or silanes may be used in the catalytic composition or added to the polymerization system. Silanes may be characterized by the formula $SiR'_{4-q}D_q$ where R' is defined as above, q is 1, 2, 3 or 4 and D is as defined above, with the proviso that there is at least one D that is a hydride.

[0053] The molar ratio of erbium metal precursor:activator employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:10 to 1:1. In a preferred embodiment of the invention mixtures of the above compounds are used, particularly a combination of a group 13 reagent and an ionic activator (i.e., those with a positive and negative charge). The molar ratio of group 13 reagent to ionic activator is preferably from 1:10,000 to 1000:1, more preferably from 1:5000 to 100:1, most preferably from 1:100 to 100:1. In a preferred embodiment, the ion forming activators are combined with a tri-alkyl aluminum, specifically trimethylaluminum, triethylaluminum, or triisobutylaluminum or with a di-alkyl aluminum hydride such as di-isobutyl aluminum hydride.

Ligands

[0054] One or more ligands are an optional addition to the catalyst composition of the erbium metal precursor and at least one activator or activating technique. The ligands useful in this invention broadly are those ligands that bind metal ions (e.g., via covalent bonds, dative bonds or combinations thereof). Ligand characteristics that can be varied include, but are not limited to, the number of coordination sites on the metal which the ligand can occupy, the charge and electronic influence of the ligand, the geometry imposed on the metal by the ligand, the geometry imposed on the ligand by the metal, *etc.* A plethora of metal-binding ligands are known in the art. *See*, for example, Collman, J.P., *et al.* PRINCIPLES AND APPLICATIONS OF ORGANOTRANSITION METAL CHEMISTRY, University Science Books, California, 1987, and references therein which are herein incorporated by reference. The metal-ligand compounds or complexes may have more than one geometry.

[0055] Generally, the coordination sites of the ligand are 1, 2, 3 or 4, and the charge on the ligands are 0, -1, -2, or -3. By "charge on the ligand," in one embodiment, it is intended that this number refer to the number of non-dative covalent bonds that could be formed with the erbium metal center. In another embodiment, "charge on the ligand" refers to the charge that one skilled in the art would assign to the ligand to balance the overall charge of the metal-ligand complex when the metal center is considered to be an ion with a positive charge that is equivalent to the oxidation state of the metal, and may be represented by M^{m+} with M being the metal and m being the oxidation state (which, e.g., for erbium is $M = \text{Er}$ and m is typically 3). Other ligands include those wherein the charge is greater than the number of sites it occupies. Due to the nature of their structure, certain ligands will have more than one possible coordination number and/or more than one possible charge. Also, a ligand may be deprotonated prior to use with the erbium metal precursor or may be deprotonated upon reaction with the erbium metal precursor, for example upon reaction with ErR_3 to eliminate RH in the process of forming the metal-ligand complex or compound.

[0056] Examples of ligands that can be used in the present invention include, but are not limited to, the following:

[0057] One-site, monoanionic ligands such as those that might form a complex like $\text{Cp}^*\text{ErR}^+\text{A}^-$ (wherein R is as defined above and A^- = anion as defined above), and

other mono-Cp systems or such as aryloxy that might form a complex like
(aryloxy)ErR⁺A⁻;

[0058] Two-site, dianionic ligands, which include, for example, mono-Cp systems where a heteroatom based ancillary ligand occupies the second site (referred to in
5 U.S. Patent No. 5,064,802, the teachings of which are incorporated herein by reference); non-Cp amide systems (referred to in U.S. Patents Nos. 5,318,935, 5,495,036 and *J. Am. Chem. Soc.*, 1996, 118:10008-10009, the teachings of which are incorporated herein by reference);

[0059] Two site, monoanionic ligands including, for example, those that might form a
10 complex like (CpL)ErR⁺A⁻ (where the L is as defined above, but is covalently linked to the cyclopentadienyl group, which may also include other substituents) and related systems (referred to in WO 96/13529, the teachings of which are incorporated herein by reference) or mono-Cp systems where a heteroatom based occupies the second site (such as European Patent Application 0 805 142 A1, WO 97/42232 and WO
15 97/42239, each of which are incorporated herein by reference).

[0060] Two site, neutral ligands;

[0061] Three site, neutral ligands;

[0062] Three site, monoanionic ligands;

[0063] Three site, dianionic ligands (an example of which is referred to in
20 *Organometallics* 1995, 14:3154-3156, which is incorporated herein by reference);

[0064] Four site, neutral, monoanionic and dianionic ligands; and

[0065] Ligands where the charge is greater than the number of sites it occupies (*see*,
for example, U.S. Patent No. 5,504,049, the teachings of which are incorporated
herein by reference).

[0066] More examples of the types of ligands described above may be found by those
25 of skill in the art in Gibson, et al., *Angew. Chem. Int. Ed.*, 1999, vol. 38, pp. 428-447, which is incorporated herein by reference.

[0067] In preferred embodiments, the coordination numbers (CN) of the ligand are
independently 1, 2, 3 or 4, and the charge on the ligands are independently 0, -1 or -2.

Preferred coordination numbers and charges are: (i) CN = 2, charge = -2; (ii) CN =
30 2, charge = -1; (iii) CN = 1, charge = -1; (iv) CN = 2, charge = 0; (v) CN = 3, charge
= -1; (vi) CN = 3, charge = -2; (vii) CN = 3, charge = 0; (viii) CN = 4, charge = 0; (ix)

CN = 4, charge = -1; (x) CN 4, charge = -2 and (xi) CN = 1, charge = 0. In other embodiments, the ligand has a charge, which is greater than the number of coordination sites it occupies on a metal ion, such as a CN = 1 and charge = -2 ligand, for example imido ligands that are referred to in Gibson et al., *Id.* Thus, the format used to describe the classes of ligands herein is where the first number refers to the coordination number and the second number refers to the ligand charge, which appears as (coordination number, charge). Therefore, a (2,-2) ligand is a CN = 2 and charge = -2 ligand.

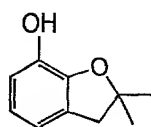
[0068] Using the (coordination number, charge) notation, the ligands useful in this invention may be characterized by the formula:

$$\{(a,0)_i (b,c)_j\}$$

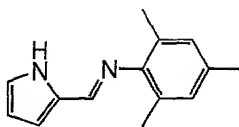
where a is the coordination number and is an integer from 1-4, b is the coordination number and is an integer from 1-4, c is the ligand charge and is -1 or -2, i is an integer from 0-5 and j is 0, 1 or 2, provided that the sum of i + j is greater than or equal to 1.

Also, when c is -1, j is 1 or 2 and when c is -2, j is 1. The first part of this formula (a,0) is directed toward neutral ligands (charge = 0) and may be provided by an atom with a lone pair of electrons (such as O, N, P, S or C with appropriate other substituents (e.g., carbenes when the atom is C)) or by a bond (such as an in an agostic interaction or a pi (π) bond). The second part of this formula (b,c) is directed toward charged ligands and may be provided by one or more atoms (such as C, S, O, N, P, B, Si, Se, As, Te, with appropriate other substituents) or by a bond (such a pi (π) bond).

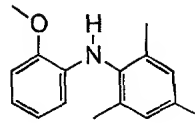
[0069] Selected examples of ligands that may be used in this invention, and showing the appropriate notation (coordination number, charge) are shown below. These ligands are shown in their protonated form, but may be de-protonated as described above.



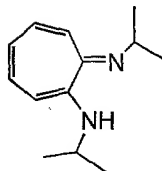
(2,-1)



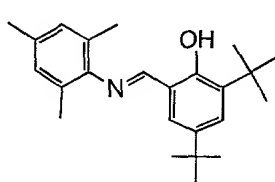
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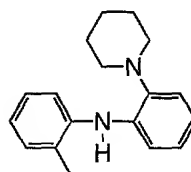
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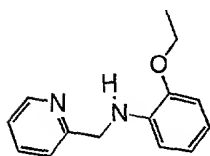
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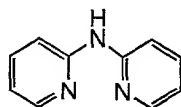
(2,-1)



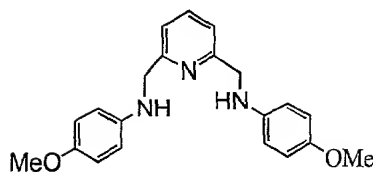
(2,-1)



(3,-1)



(3,-1)



(3,-2)

[0070] In other applications, the ligand will be mixed with a suitable metal precursor compound prior to or simultaneous with allowing the mixture to be contacted to the reactants. When the ligand is mixed with the metal precursor compound, a metal-ligand complex may be formed, which may be a catalyst. In connection with the metal complex and depending on the ligand or ligands chosen, the erbium metal complex may take the form of dimers, trimers or higher orders thereof or there may be two or more erbium atoms that are bridged by one or more ligands. Furthermore, two or more ligands may coordinate with a single erbium atom. The exact nature of the metal complex(es) or compound(s) formed depends on the exact chemistry of the ligand and the method of combining the erbium metal precursor and ligand, such that a distribution of erbium metal complexes may form with the number of ligands bound to the metal being greater or less than the number of equivalents of ligands added relative to an equivalent of erbium metal precursor.

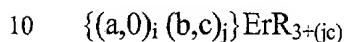
[0071] The ligands may be supported, with or without the erbium metal coordinated, on an organic or inorganic support. Suitable supports include silicas, aluminas, clays,

zeolites, magnesium chloride, polyethyleneglycols, polystyrenes, polyesters, polyamides, peptides and the like. Polymeric supports may be cross-linked or not. Similarly, the metal may be supported with or without the ligand, on similar supports known to those of skill in the art.

5

Metal Complexes

[0072] As discussed above, the erbium metal precursor may be combined with one or more ligands, and thus, an erbium metal complex or compound may be formed. Such complexes or compounds may be characterized by the formula:



where a, b, c, i, j, and R each have the above definitions and jc is the product of j multiplied by c. The coordination of the ligand or ligands to the erbium atom will be governed by those chemical principles known to those of skill in the art, including principles such as steric interactions as well as electronic configurations. If the above complex bears a charge of w, then the formula would be $[\{(a,0)_i (b,c)_j\} \text{ErR}_{3+(jc)-w}]^w$ where w is a integer that is -3, -2, -1, 1, or 2.

15

[0073] When activated with an ion forming activator (which are discussed above), the erbium metal complexes may be characterized by the formula:



20

where each of the variables in the above formula has the above definitions. Thus, for example, A may be $\text{B}(\text{C}_6\text{F}_5)_4$ as discussed above. Moreover, since some embodiments of this invention utilize one or more additional reagents (as described above), the erbium metal complexes useful in this invention may form bridged species with the group 13 or divalent or alkali metal reagents. Optionally, this complex may be charged and may be associated with a suitable counterion.

25

Monomers/Polymers

[0074] The compositions and catalysts herein may be used to polymerize olefinically or acetylenically unsaturated monomers having from 2 to 20 carbon atoms either alone or in combination. The compounds and catalysts of this invention may also usefully polymerize functionalized monomers. Monomers include olefins, diolefins and acetylenically unsaturated monomers including ethylene and C_3 to C_{20} α -olefins

30

such as propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, 1-norbornene, styrene and mixtures thereof; additionally, 1,1-disubstituted olefins, such as isobutylene, either alone or with other monomers such as ethylene or C₃ to C₂₀ α -olefins and/or diolefins. These definitions are intended to include cyclic olefins.

5 Diolefins generally comprise 1,3-dienes such as (butadiene), substituted 1,3-dienes (such as isoprene) and other substituted 1,3-dienes, with the term substituted referring to the same types of substituents referred to above in the definition section. Diolefins also comprises 1,5-dienes and other non-conjugated dienes. The styrene monomers may be unsubstituted or substituted at one or more positions on the aryl ring. The use
10 of diolefins in this invention is typically in conjunction with another monomer that is not a diolefin.

[0075] More specifically, it has been found that the erbium based catalysts of the present invention are particularly active for certain monomers, particularly α -olefins that have a chain length of C₄ or higher. Thus, the catalysts of the present invention
15 may provide higher comonomer incorporation for copolymers of ethylene and comonomers having four or more carbon atoms. In addition, the erbium based catalysts of the present invention may polymerize vinyl chloride alone (e.g., in a homopolymerization) or with other monomers (such as ethylene or C₃ to C₂₀ α -olefins). Furthermore, vinyl monomers with functional groups may also be
20 polymerized alone (e.g., in a homopolymerization) or with other monomers (such as ethylene or C₃ to C₂₀ α -olefins). Such functional group containing vinyl monomers can be characterized by the general formula H₂C=CH—FG, where FG is the functional group that contains at least one heteroatom (using the previous definition) or halogen (e.g., Cl, F, Br, etc.). Functional monomers include C₁-C₂₀ acrylates, C₁-
25 C₂₀ methacrylates, acrylic acid, methacrylic acid, maleic anhydride, vinyl acetate, vinyl ethers, acrylonitrile, acrylamide, vinyl chloride and mixtures thereof.

[0076] In some embodiments of the invention, certain types of polymerizations are excluded, including specific homopolymerizations and copolymerizations of specific monomers or monomer combinations.

30 [0077] Novel polymers, copolymers or interpolymers may be formed having unique physical and/or melt flow properties. Such novel polymers can be employed alone or with other polymers in a blend to form products that may be molded, cast, extruded or

spun. End uses for the polymers made with the catalysts of this invention include films for packaging, trash bags, bottles, containers, foams, coatings, insulating devices and household items. Also, such functionalized polymers are useful as solid supports for organometallic or chemical synthesis processes.

5

Polymerization Systems

[0078] Polymerization can be carried out in the Ziegler-Natta or Kaminsky-Sinn methodology, including temperatures of from -100°C to 300°C and pressures from atmospheric to 3000 atmospheres. Suspension, solution, slurry, gas phase or high-
10 pressure polymerization processes may be employed with the catalysts and compounds of this invention. Such processes can be run in a batch, semi-batch or continuous mode. Examples of such processes are well known in the art. A support for the catalyst may be employed, which may be inorganic (such as alumina, magnesium chloride or silica) or organic (such as a polymer or cross-linked polymer).

15 Methods for the preparation of supported catalysts are known in the art. Slurry, suspension, solution and high-pressure processes as known to those skilled in the art may also be used.

[0079] Suitable solvents for polymerization are noncoordinating, inert liquids.

Examples include straight and branched-chain hydrocarbons such as isobutane,
20 butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C₄₋₁₀ alkanes, and aromatic and alkylsubstituted aromatic compounds such as benzene, toluene, and xylene. Suitable solvents also include liquid olefins

25 which may act as monomers or comonomers including ethylene, propylene, 1-butene, butadiene, cyclopentene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, isobutylene, styrene, divinylbenzene, allylbenzene, vinyltoluene (including all isomers alone or in admixture), vinyl chloride, acrylonitrile, acrylates, vinyl acetate, methacrylates, 4-vinylcyclohexene,
30 and vinylcyclohexane. Mixtures of the foregoing are also suitable.

[0080] Other additives that are useful in a polymerization reaction may be employed, such as scavengers, promoters, etc.

Combinatorial Methodology

5 [0081] The metal complexes and compositions of this invention can be prepared and tested for catalytic activity in one or more of the above reactions in a combinatorial fashion. Combinatorial chemistry generally involves the parallel or rapid serial synthesis and/or screening or characterization of compounds and compositions of matter. U.S. Patent No. 5,985,356 and WO 98/03521, both of which are incorporated herein by reference, generally disclose combinatorial methods. In this regard, the metal precursors, ligands, complexes or compositions may be prepared and/or tested
10 in rapid serial and/or parallel fashion, e.g., in an array format. When prepared in an array format, for example, the metal precursors, activators and/or ligands may be take the form of an array comprising a plurality of compounds wherein each compound can be characterized by the general formulas described above. Typically, each member of the array will have differences so that, for example, a ligand or activator or
15 R group in a first region of the array may be different than the ligand or activator or R group in a second region of the array. Other variables may also differ from region to region in the array.

[0082] In such a combinatorial array, typically each of the plurality of compositions or complexes has a different composition or stoichiometry, and typically each
20 composition or complex is at a selected region on a substrate such that each compound is isolated from the other compositions or complexes. This isolation can take many forms, typically depending on the substrate used. If a flat substrate is used, there may simply be sufficient space between regions so that there cannot be interdiffusion between compositions or complexes. As another example, the substrate
25 can be a microtiter or similar plate having wells so that each composition or complex is in a region separated from other compounds in other regions by a physical barrier. The array may also comprise a parallel reactor or testing chamber.

[0083] The array typically comprises at least 8 compounds, complexes or compositions each having a different chemical formula, meaning that there must be at
30 least one different atom or bond differentiating the members in the array or different ratios of the components referred to herein (with components referring to erbium metal precursors, activators, group 13 reagents, solvents, monomers, supports, etc.).